Liquid-crystal medium, and electro-optical display containing the liquid-crystal medium

The present invention relates to active matrix-addressed liquid-crystal displays (AMDs or AMLCDs), in particular those which use an active matrix of thin-film transistors (TFTs) or varistors. In addition, the present application relates to liquid-crystal media for use in such displays. Such AMDs can use various active electronic switching elements. The most widespread are displays using three-pole switching elements. These are also preferred in the present invention. Examples of such three-pole switching elements are MOS (metal oxide silicon) transistors and the abovementioned TFTs or varistors. In the case of TFTs, various semiconductor materials, predominantly silicon or cadmium gelenside, are used. In particular, polycrystalline silicon or amorphous silicon is used. In contrast to the three-pole electronic switching elements, matrices of 2-pole switching elements, such as, for example, MIM (metal insulator metal) diodes, ring diodes or back-to-back diodes, can be employed in AMDs. However, these are, as also explained in greater detail below, not preferred owing to the inferior electro-optical properties achieved by the AMDs.

In liquid-crystal displays of this type, the liquid crystals are used as dielectrics whose optical properties change reversibly on application of an electric voltage. Electro-optical displays which use liquid crystals as media are known to the person skilled in the art. These liquid-crystal displays use various electro-optical effects. The most common of these are the TN effect (twisted nematic, having a nematic structure which is twisted by about 90°), the STN effect (supertwisted nematic) and the SBE effect (supertwisted birefringence effect). In these and similar electro-optical effects, liquid-crystalline media of positive dielectric anisotropy ($\Delta\varepsilon$) are used.

Since the operating voltage should be kept as low as possible in displays in general, including in displays using these effects, use is made of liquid-crystal media of large dielectric anisotropy which are generally composed predominantly of dielectrically positive liquid-crystal compounds and contain at most smaller/lower proportions of dielectrically neutral compounds.

Besides these electro-optical effects, which require liquid-crystal media of positive dielectric anisotropy, there are other electro-optical effects which use liquid-crystal media of negative dielectric anisotropy, such as, for example, the ECB effect (electrically controlled birefringence) and its sub-forms DAP (deformation of aligned phases), VAN (vertically aligned nematics) and CSH (colour super homeotropics).

The IPS effect (in-plane switching), which has been increasingly used recently, can use both dielectrically positive and dielectrically negative liquid-crystal media, similarly to guest/host displays, which, depending on the display mode used, can use dyes either in dielectrically positive or in dielectrically negative media.

The liquid-crystal media employed in the abovementioned liquid-crystal displays and all liquid-crystal displays utilizing similar effects generally consist predominantly and usually even very substantially of liquid-crystal compounds having the corresponding dielectric anisotropy, i.e. compounds of positive dielectric anisotropy in the case of dielectrically positive media and compounds of negative dielectric anisotropy in the case of dielectrically negative media.

In the respective types of media (dielectrically positive or dielectrically negative), at best significant amounts of dielectrically neutral liquid-crystal compounds are typically employed, since in general the liquid-crystal displays must have the lowest possible addressing voltages. For this reason, liquid-crystal compounds having the opposite sign of the dielectric anisotropy to the dielectric anisotropy of the medium are generally employed extremely sparingly or not at all.

An exception is formed here by liquid-crystalline media for MIM displays (metal insulator metal) [J.G. Simmons, Phys. Rev. Vol. 155 No. 3, pp. 657-660; K. Niwa et al., SID 84 Digest, pp. 304-307, June 1984], in which the liquid-crystal media are addressed on an active matrix of thin film transistors (TFD, thin film diodes). In this type of addressing, which utilizes the non-linear characteristic line of diode switching, a storage capacitor cannot be charged together with the electrodes of the liquid-crystal display elements (pixels), in contrast to TFT displays. Thus, in order to minimize the effect of voltage drop during the addressing cycle, the highest possible base value of the dielectric constant is necessary. In dielectrically positive media, as employed, for example, in MIM-TN displays, the dielectric constant perpendicular to the molecular axis ($\varepsilon_{\perp}$) must thus be as large as possible, since it determines the base capacity of the pixel. To this end, as in WO 93/01253, EP 0 663 502 and DE 195 21 483, compounds of negative dielectric anisotropy are used in the dielectrically positive liquid-crystal media, besides dielectrically positive compounds.

During charging of the electrodes of the pixel by TFT addressing, the voltage present is shifted by a DC offset voltage (ΔV) by the parasitic capacitance between the gate and source of the TFT. ΔV is

proportional to the inverse value of the pixel capacitance (C_{pix}). It can be seen from this that if the pixel capacitance is relatively large both in the on and also in the partly off and in particular in the semi-off state, the undesired effect is reduced and ΔV becomes smaller.

EP 0 394 419 proposes dielectrically positive liquid-crystal media for active matrix displays based on dielectrically neutral and dielectrically positive liquid-crystal compounds, which may optionally contain dielectrically negative compounds. Although EP 0 394 419 proposes a number of examples of dielectrically negative liquid-crystal compounds, this patent application gives, with Example 22, only one of a total of 72 examples which comprises a dielectrically negative compound, and even here only in a very small proportion of 4%.

The liquid-crystal media of the prior art have relatively low low-temperature stabilities. Thus, the nematic phases frequently extend only down to -20°C and in some cases even only down to 0°C. In addition, the threshold voltages (V_{10}) are also simultaneously relatively high, usually even greater than 2 V. The majority of the liquid-crystal media of the prior art have relatively large values for Δn, frequently greater than 0.10, in some cases even significantly greater than 0.10, and predominantly greater than 0.09. However, such large Δn values are not particularly advantageous for TN displays operated at the first Gooch and Tarry transmission minimum, i.e. at an optical retardation $d \cdot \Delta n$ of approximately 0.5 μm, as employed in order to achieve good, low viewing-angle dependence of the contrast (DE 30 22 818). Such large Δn values require very small layer thicknesses to be achieved, which, although favourable for the response times observed, result, however, in low production yields.

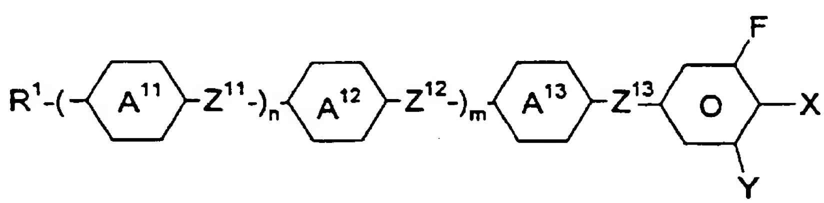
There thus was and is a great demand for liquid-crystal media which do not have the disadvantages of the media of the prior art, or at least do so to a significantly reduced extent, and which simultaneously have reduced cross-talk between adjacent pixels, in particular between on pixels and adjacent off pixels.

Furthermore, so-called flicker is observed in some active matrix addressed displays. This effect is observed both in displays in TN mode and also, in particular, in those VAN mode. This interfering effect is attributed, at least in part, to the voltage offset ΔV of the voltage present on the LC cell, which is itself caused by the varying polarity of the drain voltage at the transistors of the active matrix.

This is achieved by using the liquid-crystal media according to the invention, which enable a small difference in the capacitances of adjacent on and off pixels.

The liquid-crystal media according to the invention comprise

a) one or more dielectrically positive compound(s) of the formula I

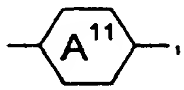


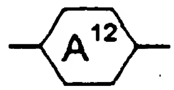
I

in which

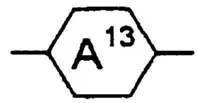
R^1 is alkyl or alkoxy having 1 to 7 carbon atoms, alkoxyalkyl, alkenyl or alkenyloxy having 2 to 7 carbon atoms,

Z^{11}, Z^{12} and Z^{13} are each, independently of one another, $-CH_2-CH_2-$, $-CH=CH-$, $-C\equiv C-$, $-COO-$ or a single bond,

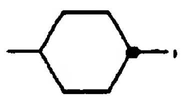
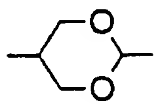
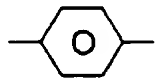
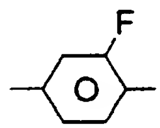




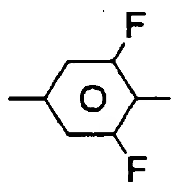
and



are each, independently of one another,

or

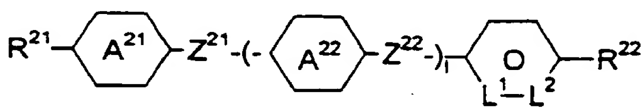


X is F, OCF_2H or OCF_3,

where, in the case where X = F or OCF_2H, Y is F, and in the case where X = OCF_3, Y is H or F, and

n and m are each, independently of one another, 0 or 1;

b) one or more dielectrically negative compound(s) of the formula II

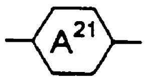


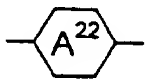
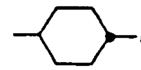
II

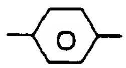
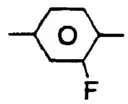
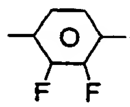
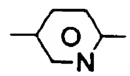
in which

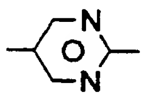
R^{21} and R^{22} are each, independently of one another, as defined for R^1 under the formula I, -

Z^{21} and Z^{22} are each, independently of one another, as defined for Z^{11} above under the formula I,

 and

 are each, independently of one another, ,

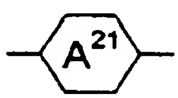
, , ,  or

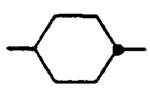
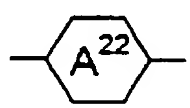
,

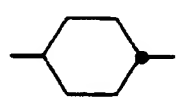
L^1 and L^2 are both C-F or one of the two is N and the other is C-F, and

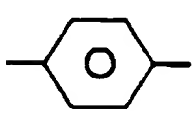
l is 0 or 1;

X is preferably F or OCF_3, particularly preferably F; R^{22} is preferably alkyl or alkoxy having 1-7 carbon atoms, and L^1 and L^2 are preferably both C-F.

 is particularly preferably

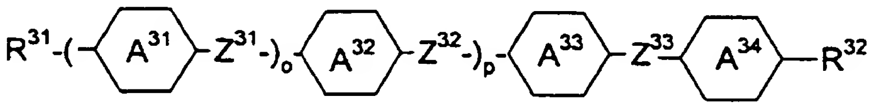
, and , if present,

is particularly preferably  or



and optionally

c) one or more dielectrically neutral compound(s) of the formula III

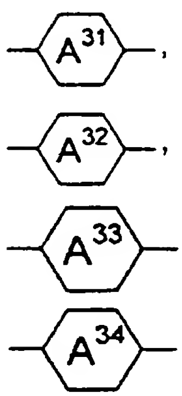


III

in which

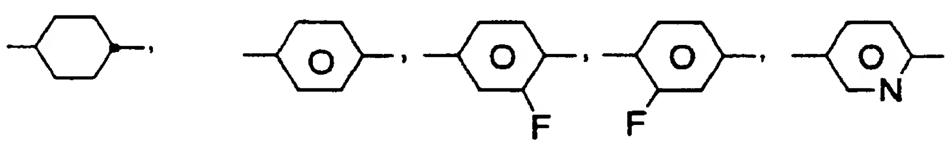
R^{31} and R^{32} are each, independently of one another, as defined for R^1 above under the formula I, and

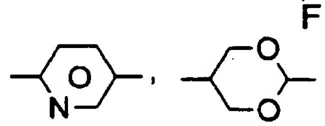
Z^{31}, Z^{32} and Z^{33} are each, independently of one another, $-CH_2CH_2-$, $-CH=CH-$, $-CH_2O-$, $-OCH_2-$, $-CF_2O-$, $-OCF_2-$, $-COO-$ or a single bond, and, if desired, one of Z^{31}, Z^{32} and Z^{33} is $-CF_2CF_2-$,



and

are each, independently of one another,





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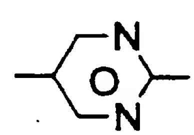
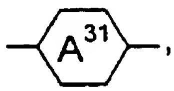


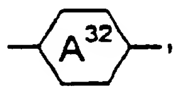
and

o and p, independently of one another, are 0 or 1,

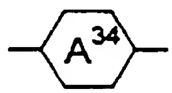
but preferably

R^{31} and R^{32} are each, independently of one another, alkyl or alkoxy having 1-5 carbon atoms or alkenyl having 2-5 carbon atoms,

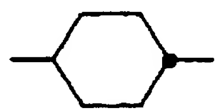




and



are each, independently of one another,



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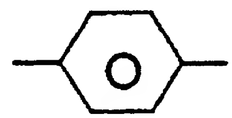
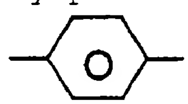
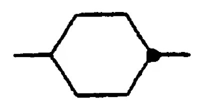
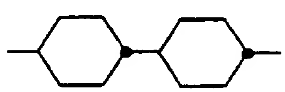


and very particularly preferably at least two of these rings are  and/or ,

where two adjacent rings are very particularly preferably directly linked and are preferably



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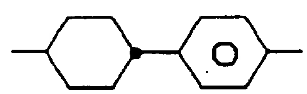
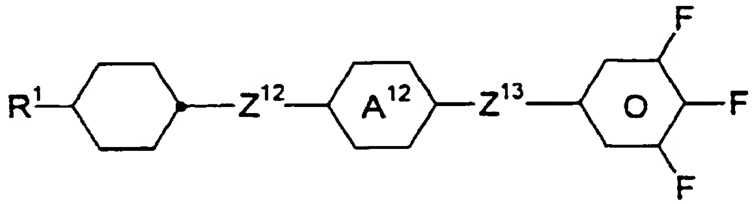
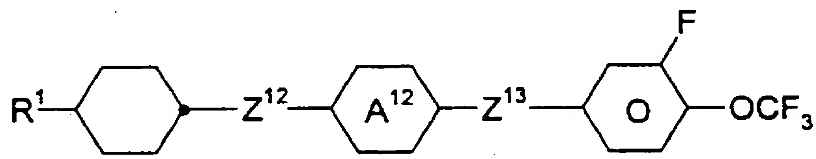
.

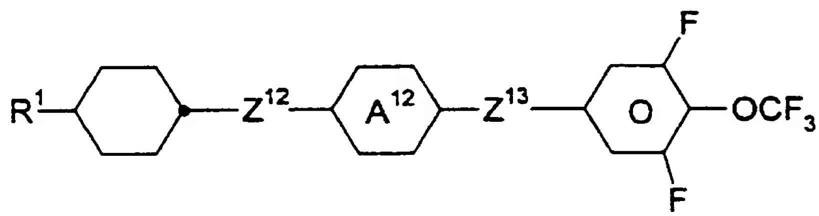
The liquid-crystal media preferably comprise one or more compounds selected from the group of compounds of the formulae I1 to I4:



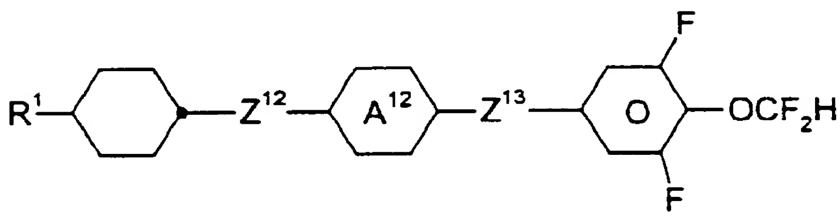
I1



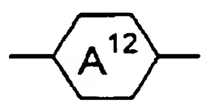
I2



I3

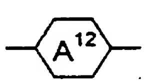
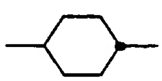
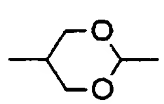
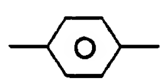
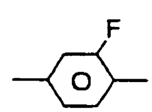


I4

in which R^1, Z^{12}, Z^{13} and  are as defined above for formula I, but preferably

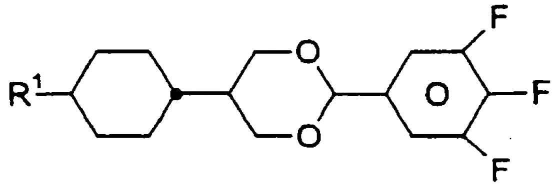
R^1 is alkyl having 1-7 carbon atoms or alkenyl having 2-7 carbon atoms, preferably vinyl or 1E-alkenyl,

one of Z^{12} and Z^{13} is a single bond and the other is $-CH_2CH_2-$, -COO- or a single bond, and

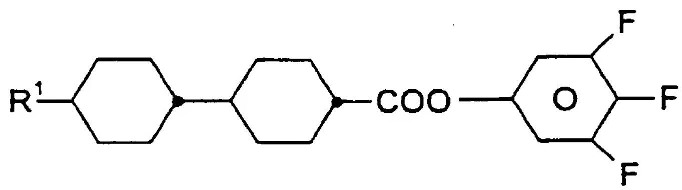
 is , ,  or .

The liquid-crystal media particularly preferably comprise one or more compounds selected from the group

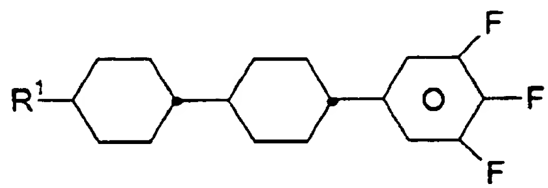
of compounds of the formulae I1a to I1e, I2a to I2e, I3a to I3e and I4a to I4e:



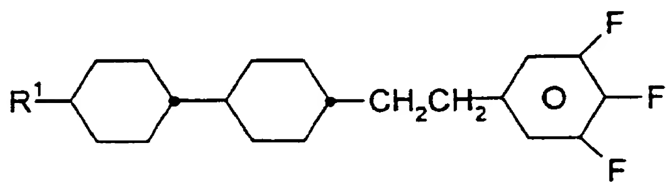
I1a



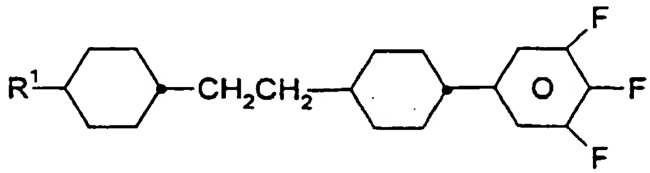
I1b



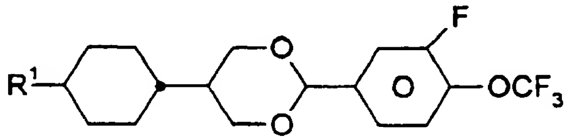
I1c



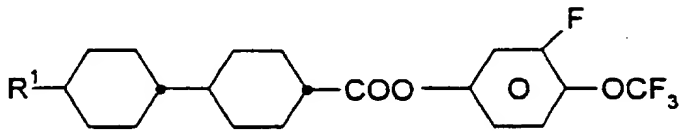
I1d



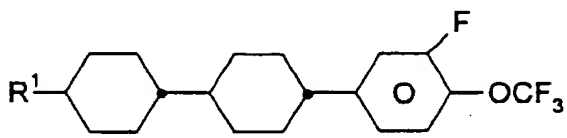
I1e



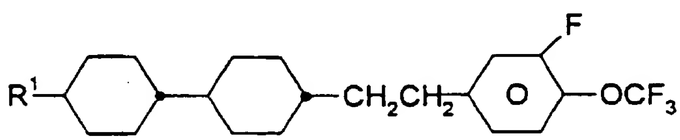
I2a



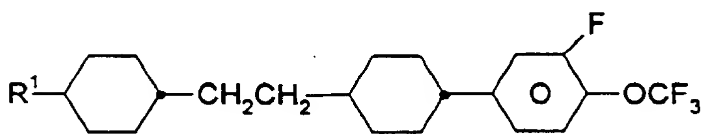
I2b



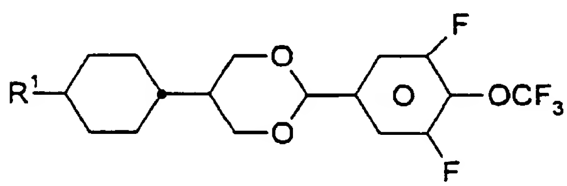
I2c



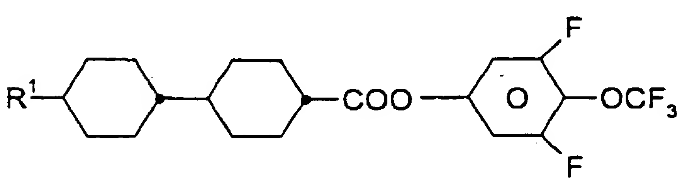
I2d



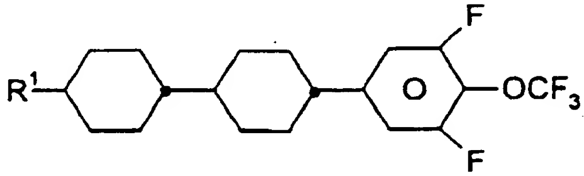
I2e



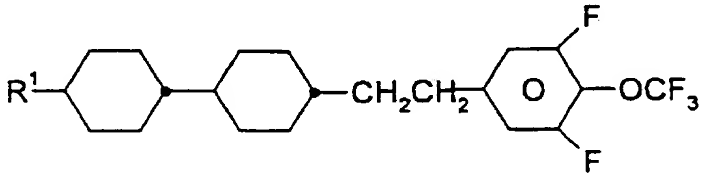
I3a



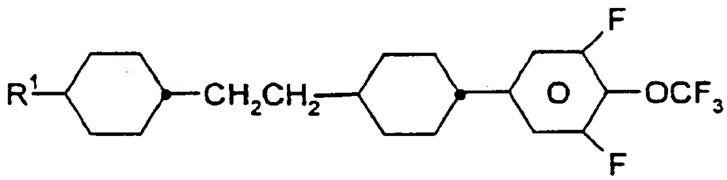
I3b



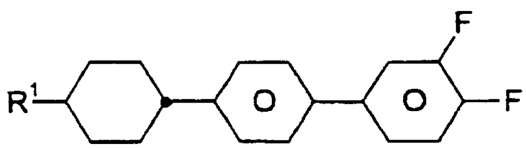
I3c



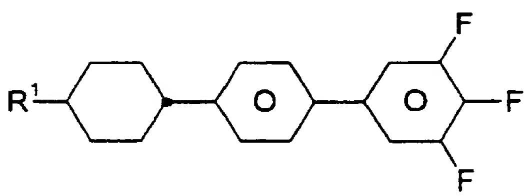
I3d



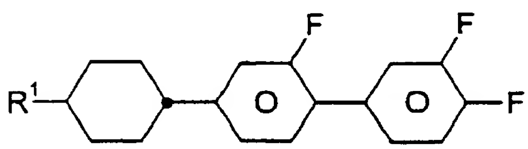
I3e



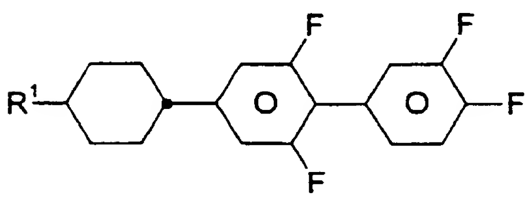
I4a



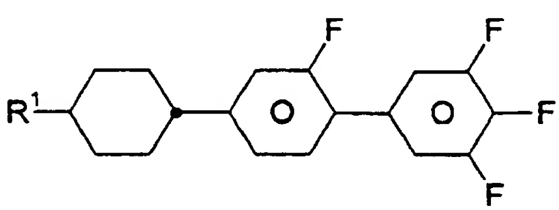
I4b



I4c



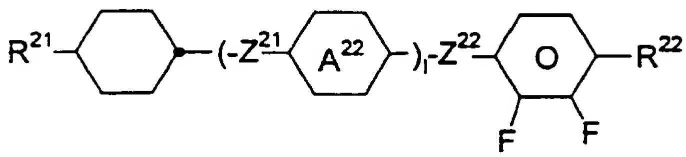
I4d



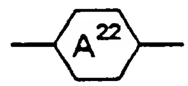
I4e

in which R^1 is as defined above under the formula I and is preferably as defined above under the formula I1. R^1 is in particular ethyl, n-propyl, n-butyl or n-pentyl.

The liquid-crystal medium preferably comprises one or more compounds of the formula II1

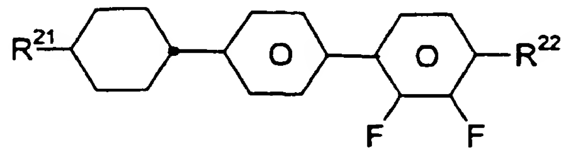


II1

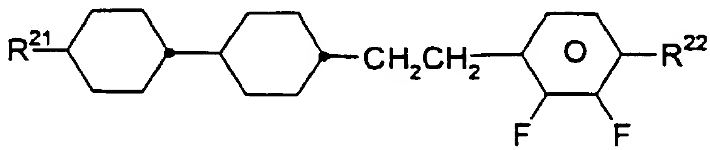
in which R^{21}, R^{22}, Z^{21}, Z^{22}, 

and l are each as defined above under the formula II. R^{21} is preferably alkyl having 1-5 carbon atoms, R^{21} is preferably alkyl or alkoxy, each having 1 to 5 carbon atoms, and Z^{22} and Z^{21}, if present, are preferably a single bond.

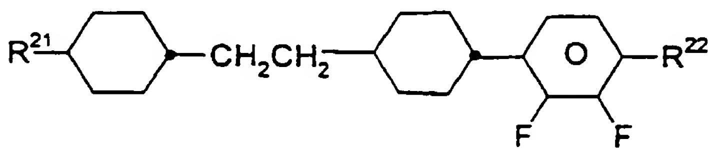
Sub A1 The liquid-crystal media particularly preferably comprise one or more compounds selected from the group of compounds of the formulae II1a to II1e:



II1c



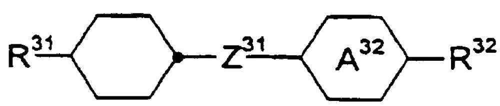
II1d



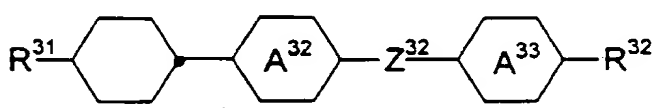
II1e

in which R^{21} and R^{22} are as defined above under the formula II and are preferably as defined above under the formula II1.

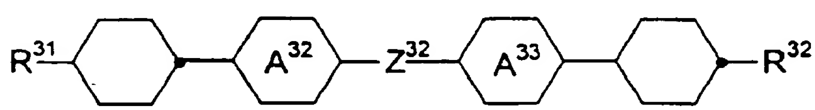
The liquid-crystal medium particularly preferably comprises one or more compounds selected from the group consisting of the compounds of the formulae III1 to III3:



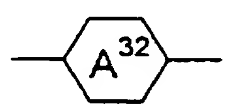
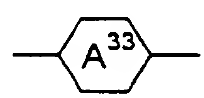
III1



III2



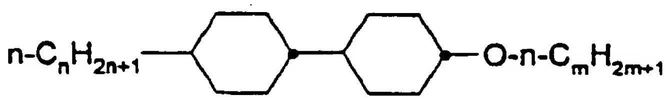
III3

in which R^{31}, R^{32}, Z^{31}, Z^{32},  and 

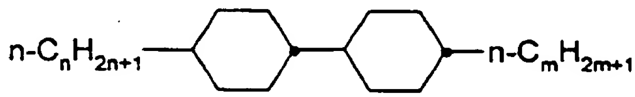
are each as defined above under the formula III.

The liquid-crystal medium particularly preferably comprises one or more compounds selected from the group

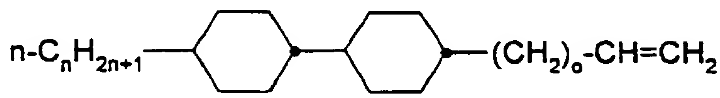
consisting of the compounds of the formulae III1a to III1d, III2a to III2e, III3a to III3c and III4a:



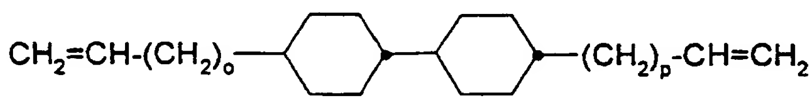
III1a



III1b

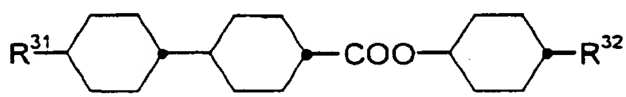


III1c

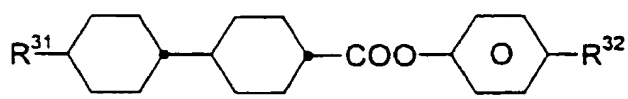


III1d

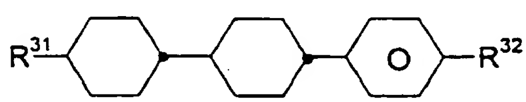
in which n and m are each, independently of one another, from 1 to 5, and o and p are each, both independently thereof and independently of one another, from 0 to 3,



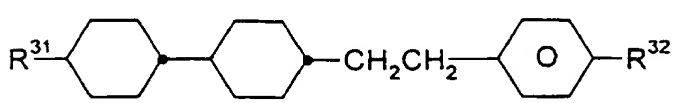
III2a



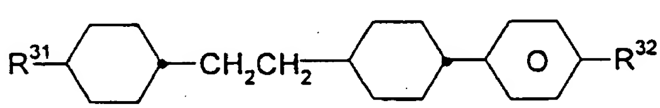
III2b



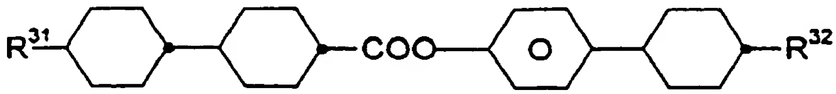
III2c



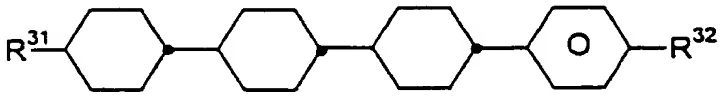
III2d



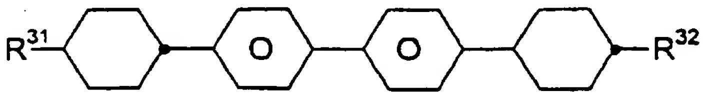
III2e



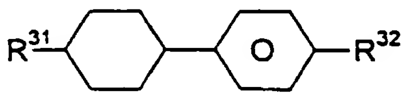
III3a



III3b



III3c



III4a

in which R^{31} and R^{33} are each as defined above under the formula III1, and the phenyl rings may optionally be fluorinated, but not in such a way that the compounds are identical to those of the formula II and their subformulae. R^{31} is preferably n-alkyl having 1 to 5 carbon atoms, particularly preferably having 1 to 3 carbon atoms, and R^{32} is preferably n-alkyl or n-alkoxy having 1 to 5 carbon atoms or alkenyl having 2 to 5 carbon atoms. Of these, particular preference is given to compounds of the formulae III1a to III1d.

In a preferred embodiment, the liquid-crystal media according to the invention comprise in total, based on the mixture as above, from 40% to 90% of compounds of the formula I, from 5% to 40% of compounds of the formula II and from 0% to 40% of compounds of the formula III.

The term compounds here means both one and a plurality of compounds. The individual compounds here are employed in concentrations of from 1% to 30%, preferably from 2% to 30%, particularly preferably from 4% to 16%.

In a preferred embodiment, the liquid-crystal media particularly preferably comprise in total

from 50% to 70% of compounds of the formula I,
from 5% to 30% of compounds of the formula II and
from 10% to 40% of compounds of the formula III.

In this embodiment, the liquid-crystal media very particularly preferably comprise in total

from 52% to 65% of compounds of the formula I,
from 10% to 25% of compounds of the formula II and
from 15% to 35% of compounds of the formula III.

In a particularly preferred embodiment, which may be identical, and preferably is identical, to the preferred embodiments described above for the preferred concentration ranges, the liquid-crystal media comprise

- one or more compounds of the formula I1a and/or
  - one or more compounds of the formula I1b, and

- one or more compounds of the formula II1a and/or
  - one or more compounds of the formula II1c
    the latter alternative being preferred, and

- one or more compounds selected from the group consisting of the compounds of the formulae III1a to III1c and/or
  - one or more compounds selected from the group consisting of the compounds of the formulae III2 and III3, and

- one or more compounds selected from the group consisting of the compounds of the formulae I1c to I1e, preferably Ic, and/or

  - one or more compounds selected from the group consisting of the compounds of the formulae I4a to I4e, preferably from the group consisting of the formulae I4b and I4e, particularly preferably both of the formula I4b and also I4e, and

- one or more compounds of the formula II, preferably selected from the group of compounds of the formulae II1a and II1c.

Particularly preferred liquid-crystal media here are those which comprise

- one or more compounds of the formula I1a, in particular, in each case per compound, in concentrations of from 6% to 14%,

- one or more compounds of the formula I1b, in particular, in each case per compound, in concentrations of from 4% to 18%,

- one or more compounds of the formula II1a, in particular, in each case per compound, in concentrations of from 3% to 10%,

- one or more compounds of the formula II1c, in particular, in each case per compound, in concentrations of from 3% to 12%, preferably in each case at least one compound in which R^{21} is alkyl having 1 to 3 carbon atoms and R^{22} is alkoxy having 1 to 3 carbon atoms, and in which R^{23} is alkyl having 1 to 3 carbon atoms and R^{32} is alkyl having 1 to 3 carbon atoms,

- one or more compounds of the formulae III1a and/or III1c, in particular in concentrations of from 4% to 15% per compound, preferably in each case at least one compound of each of the formulae III1a and III1c, and

- one or more compounds of the formula III2a.

The liquid-crystal media according to the invention preferably have nematic phases of in each case at least

from -20°C to 80°C, preferably from -30°C to 80°C, very particularly preferably from -40°C to 85°C (≥90°C). The term "having a nematic phase" here means firstly that no smectic phase and no crystallization are observed at low temperatures at the corresponding temperature, and secondly that no clearing occurs during heating from the nematic phase. The investigation at low temperatures is carried out in a flow viscometer at the corresponding temperature, and checked by storage in test cells having an appropriate layer thickness for electro-optical use, for at least 100 hours. At high temperatures, the clearing point is measured by conventional methods in capillaries.

The liquid-crystal media according to the invention are furthermore characterized by low optical anisotropy values. The birefringence values are less than or equal to 0.10, preferably less than or equal to 0.08, very particularly preferably less than or equal to 0.07.

In addition, the liquid-crystal media according to the invention have small threshold voltage values of less than or equal to 2.0 V, preferably less than or equal to 1.9 V, particularly preferably less than or equal to 1.7 V, very particularly preferably less than or equal to 1.5 V.

These preferred values for the individual physical properties are also maintained when in each case combined with one another. Thus, media according to the invention have, in particular, the following property combinations:

SUB A2

	Phase	Δn	Threshold voltage/V
According to the invention	≤ -20 to ≥ 80	≤ 0.01	≤ 1.9
Preferred	≤ -30 to ≥ 90	≤ 0.08	≤ 1.7
Particularly preferred	≤ -40 to ≥ 80	≤ 0.07	≤ 1.5

where, as in the entire application, "≤" means less than or equal to and "≥" means greater than or equal to.

For displays containing liquid crystals of negative Δε, in particular for ECB and particularly preferably for VAN displays, the liquid-crystal media preferably comprise in total from 0.5% to 38% of compounds of the formula I, from 20% to 95% of compounds of the formula II and from 5% to 50% of compounds of the formula III.

These liquid-crystal media particularly preferably comprise

from 1% to 15% of compounds of the formula I,
from 50% to 85% of compounds of the formula II and
from 10% to 40% of compounds of the formula III.

These liquid-crystal media very particularly preferably comprise

from 1% to 10% of compounds of the formula I,
from 60% to 80% of compounds of the formula II and
from 20% to 35% of compounds of the formula III.

Independently of the abovementioned amount limits for the compounds of the formulae II and III, compounds of the formula I are employed in these liquid-crystal media in concentrations of up to 7%, preferably up to 5%.

In a preferred embodiment, these liquid-crystal media comprise

- one or more compounds of the formula I1c and
- one or more compounds of the formula II1a and/or preferably
  - one or more compounds of the formula II1c, and
- one or more compounds of the formulae III1c and/or III1d and/or
  - one or more compounds of the formula III1b and/or
  - one or more compounds of the formula III4a.

The abovementioned preferred concentration ranges particularly preferably also apply to this preferred combination of compounds.

These liquid-crystal media according to the invention of negative Δε have nematic phases from -20°C to +70°C, preferably from -30°C to +70°C, particularly preferably from -30°C to +80°C.

Particular preference is given to media having the following property combination:

	Phase	Δn	Freedericksz threshold/V
According to the invention	≤ -20 to ≥ 70	≤ 0.09	≤ 2.0
Preferred	≤ -30 to ≥ 70	≤ 0.08	≤ 1.9
Particularly preferred	≤ -40 to ≥ 80	≤ 0.075	≤ 1.9

In the present application, the term "dielectrically positive compounds" is taken to mean compounds having a Δε of > 1.5, the term "dielectrically neutral compounds" is taken to mean compounds in which -1.5 ≤ Δε ≤ 1.5, and "dielectrically negative compounds" is taken to mean compounds in which Δε is < -1.5. The dielectric

anisotropy of the compounds is determined here by dissolving 10% of the compounds in a liquid-crystalline host and determining the capacitance of this mixture at 1 kHz in at least one test cell each with a thickness of 10 μm and a homeotropic and homogeneous surface alignment. The measurement voltage is typically from 0.5 V to 1.0 V, but is always less than the capacitive threshold of the respective liquid-crystal mixture.

The host mixture used for dielectrically positive compounds is ZLI-4792 and that used for dielectrically neutral and dielectrically negative compounds is ZLI-3086, both from Merck KGaA, Germany. The values for the respective compounds to be investigated are obtained from the change in dielectric constants of the host mixture after addition of the compound to be investigated and extrapolation to 100% of the compound employed.

The term threshold voltage in the present application relates to the optical threshold for 10% relative contrast (V_{10}), unless explicitly stated otherwise.

However, in relation to the liquid-crystal mixtures of negative dielectric anisotropy, the term threshold voltage is used for the capacitive threshold voltage (V_0), also known as the Freedericksz threshold, unless explicitly stated otherwise.

All concentrations in this application, unless explicitly stated otherwise, are given in per cent by weight and relate to the corresponding mixture as a whole. All physical properties are and have been determined as described in "Merck Liquid Crystals, Physical Properties of Liquid Crystals", Status Nov. 1997, Merck KGaA, Germany, and apply to a temperature of 20°C, unless explicitly stated otherwise. Δn is determined at 589 nm and $\Delta\varepsilon$ at 1 kHz. The threshold voltages and the other electro-optical properties were

determined in test cells produced at Merck KGaA, Germany, using white light in a commercial measuring instrument from Otsuka, Japan. To this end, cells were used, depending on Δn of the liquid crystals, with a thickness corresponding to the 1st Gooch and Tarry transmission minimum. The optical retardation $d \cdot \Delta n$ of the cells was thus about 0.50 μm. The cells were operated in so-called "normally white mode" with a polarizer transmission direction perpendicular to the respective adjacent rubbing directions. The characteristic voltages were all determined with perpendicular observation. The threshold voltage was given as V_{10} for 10% relative contrast, the central limit voltage V_{50} for 50% relative contrast and the saturation voltage V_{90} for 90% relative contrast.

In the liquid-crystal media of negative dielectric anisotropy, the threshold voltage was determined as the capacitive threshold V_0 (also known as the Freedericksz threshold) in cells containing liquids which had been homeotropically aligned by lecithin.

The DC offset voltage (ΔV) is determined as follows: the test pixel is addressed using a TFT, and the voltage shift is measured. The following equation applies:

$$\Delta V = V_{gate} \cdot C_{gs} / (C_{gs} + C_{st} + C_{LC}),$$

where

C_{gs} denotes the parasitic capacitance between the gate and source,

C_{st} denotes the capacitance of the storage capacitor,

C_{LC} denotes the capacitance of the LC layer of the pixel, and

V_{gate} denotes the gate voltage.

The liquid-crystal media according to the invention may, if necessary, also comprise further additives and

chiral dopants in conventional amounts. The amount of these additives employed is in total from 0% to 10%, based on the amount of mixture as a whole, preferably from 0.1% to 6%. The concentrations of the individual compounds employed are preferably from 0.1 to 3%. The concentration of these and similar additives is not taken into account when giving the concentrations and the concentration ranges of the liquid-crystal compounds in the liquid-crystal media.

The compositions consist of a plurality of compounds, preferably from 3 to 30, particularly preferably from 6 to 20, very particularly preferably from 10 to 16 compounds, which are mixed in a conventional manner. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, expediently at elevated temperature. If the temperature selected is above the clearing point of the principal constituent, completion of the dissolution operation is particularly easily observed. However, it is also possible to prepare the liquid-crystal mixtures in other conventional ways, for example by using premixtures or from a so-called "multibottle system".

By means of suitable additives, the liquid-crystal phases according to the invention can be modified in such a way that they can be employed in any type of TN-AMD that has been disclosed hitherto.

The examples below serve to illustrate the invention without representing a limitation. In the examples, the melting point T (C,N), the transition from the smectic (S) to the nematic (N) phase T (S,N) and the clearing point T (N,I) of a liquid-crystal substance are given in degrees Celsius. The percentage data denote percent by weight.

Unless stated otherwise, all percentages above and below are per cent by weight, and the physical properties are the values at 20°C, unless explicitly stated otherwise.

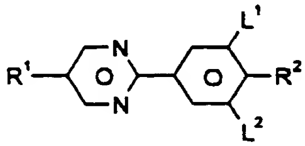
All temperature values given in this application are °C and all temperature differences are correspondingly difference degrees, unless explicitly stated otherwise.

In the present application and in the examples below, the structures of the liquid-crystal compounds are indicated by means of acronyms, the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals C_nH_{2n+1} and C_mH_{2m+1} are straight-chain alkyl radicals having n and m carbon atoms respectively. The coding in Table B is self-evident. In Table A, only the acronym for the parent structure is given. In individual cases, the acronym for the parent structure is followed, separated by a hyphen, by a code for the substituents R^1, R^2, L^1 and L^2:

Code for R^1, R^2, L^1, L^2	R^1	R^2	L^1	L^2
nm	C_nH_{2n+1}	C_mH_{2m+1}	H	H
nOm	C_nH_{2n+1}	OC_mH_{2m+1}	H	H
nO.m	OC_nH_{2n+1}	C_mH_{2m+1}	H	H
n	C_nH_{2n+1}	CN	H	H
nN.F	C_nH_{2n+1}	CN	H	F
nF	C_nH_{2n+1}	F	H	H
nOF	OC_nH_{2n+1}	F	H	H
nCl	C_nH_{2n+1}	Cl	H	H
nF.F	C_nH_{2n+1}	F	H	F
nmF	C_nH_{2n+1}	C_mH_{2m+1}	F	H
nCF_3	C_nH_{2n+1}	CF_3	H	H
$nOCF_3$	C_nH_{2n+1}	OCF_3	H	H
$nOCF_2$	C_nH_{2n+1}	$OCHF_2$	H	H
nS	C_nH_{2n+1}	NCS	H	H
rVsN	$C_rH_{2r+1}-CH=CH-C_sH_{2s}-$	CN	H	H
rEsN	$C_rH_{2r+1}-O-C_sH_{2s}-$	CN	H	H

nAm	C_nH_{2n+1}	$COOC_mH_{2m+1}$	H	H
nF.Cl	C_nH_{2n+1}	Cl	H	F

<u>**Table A:**</u>



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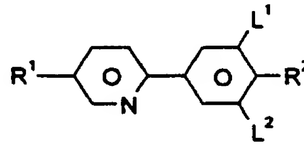
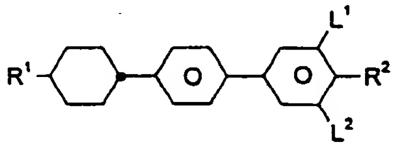


PYRP



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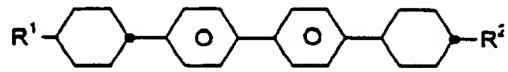

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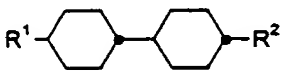

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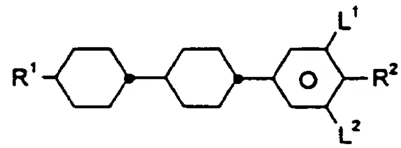

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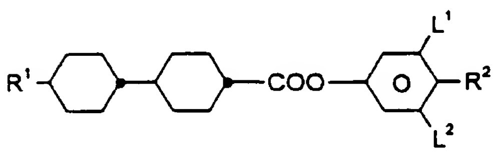

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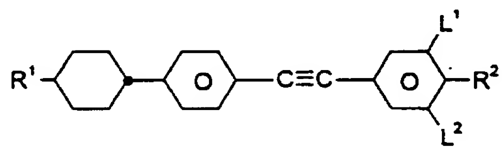

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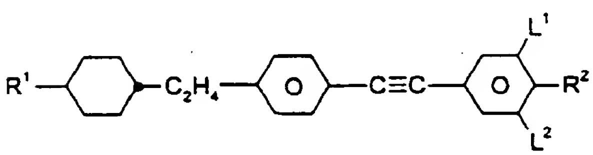

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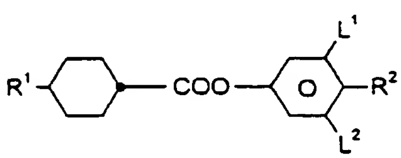

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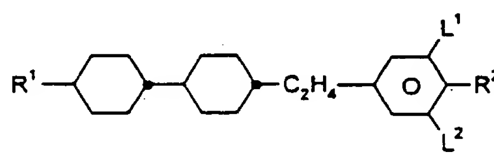

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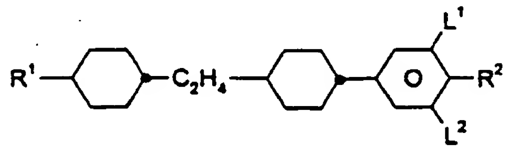

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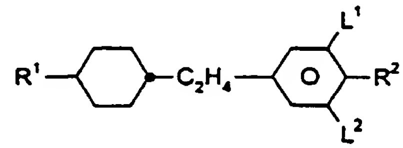

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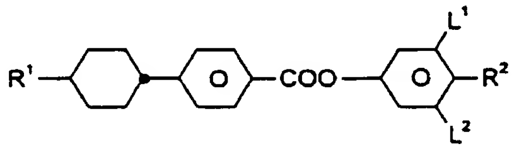

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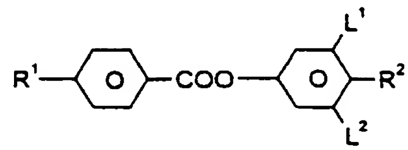

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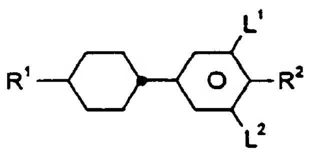
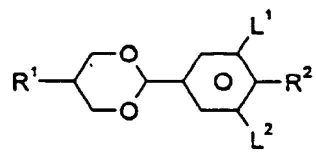


PCH



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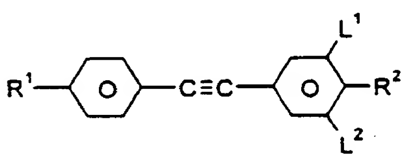

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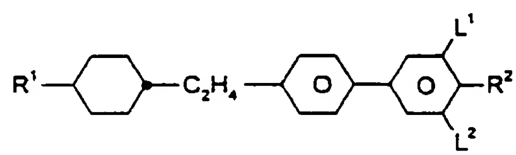

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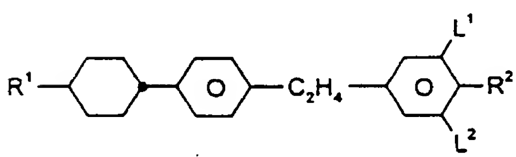

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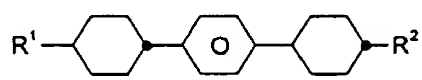

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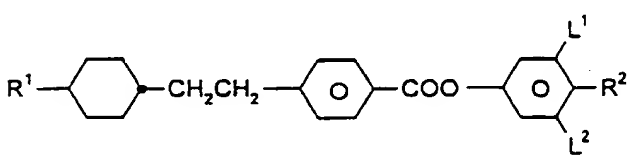

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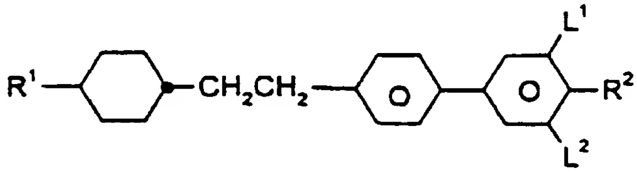

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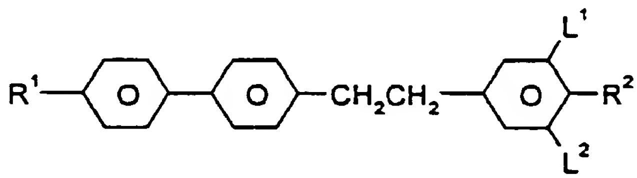

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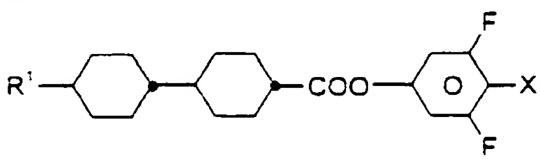

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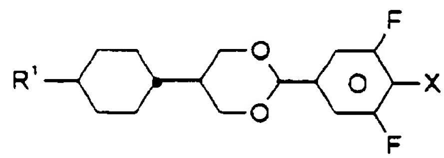

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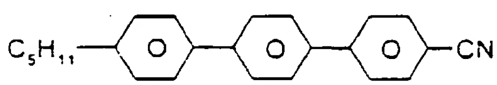

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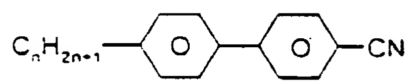

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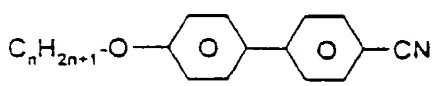
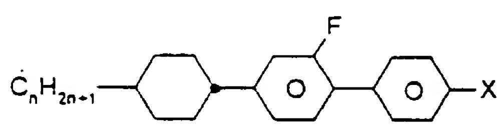


M3n



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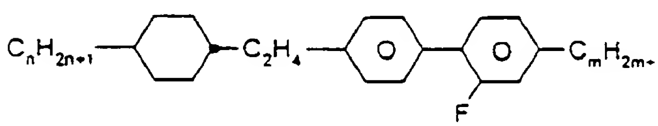
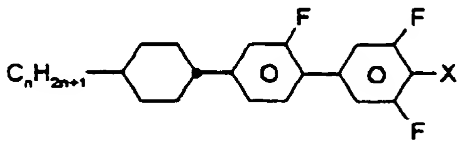


Inm



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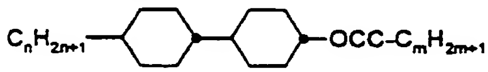

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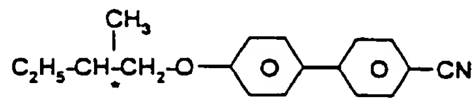

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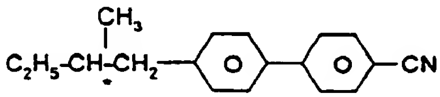

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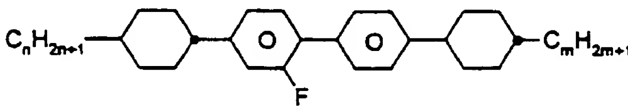

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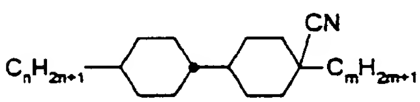

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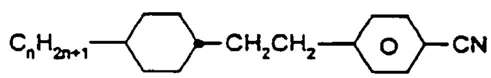

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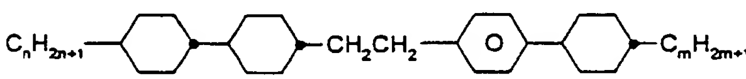

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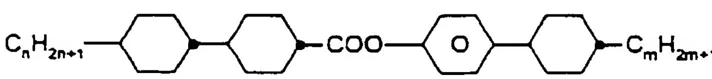

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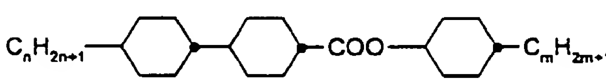

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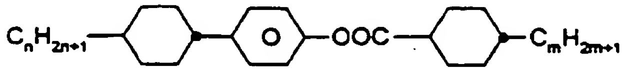

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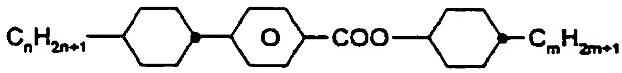
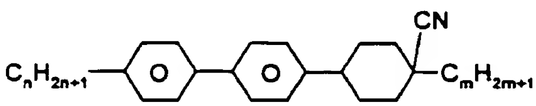


HH-nm



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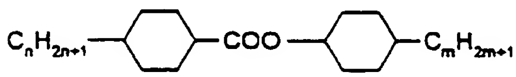

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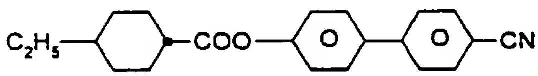

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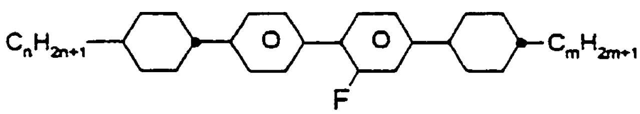
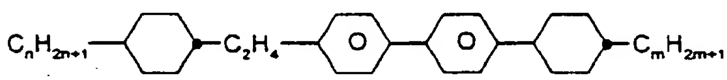


CBC-nmF



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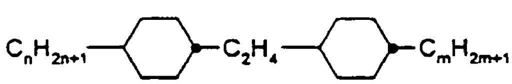

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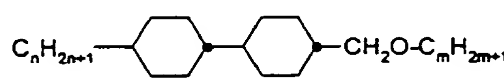

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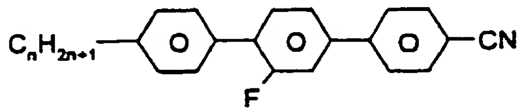

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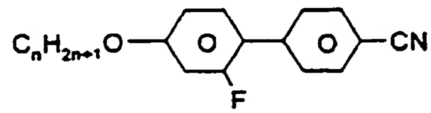

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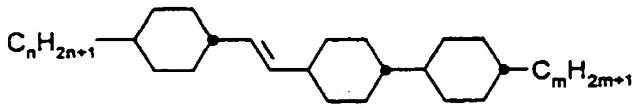
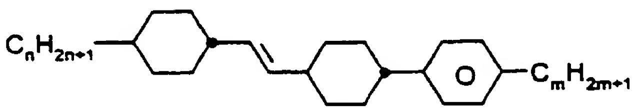


CVCC-n-m



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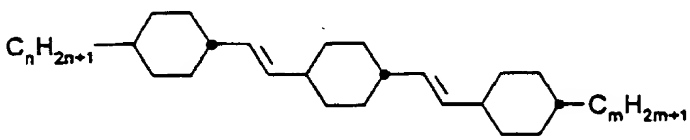
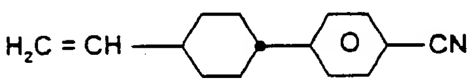


CVCVC-n-m



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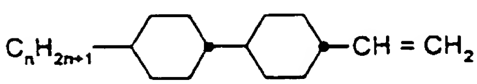
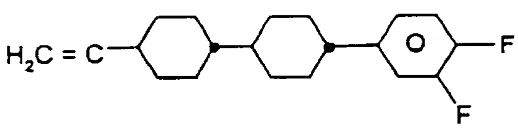
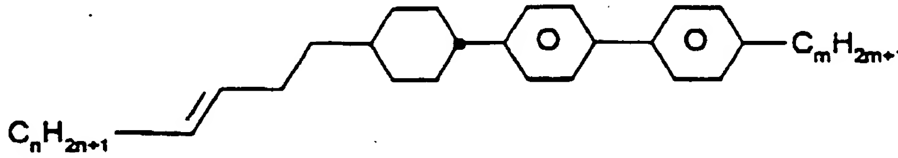


CC-n-V



CCG-V-F



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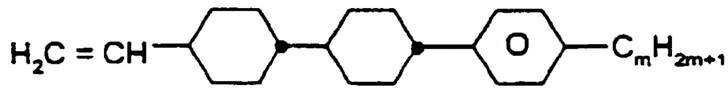

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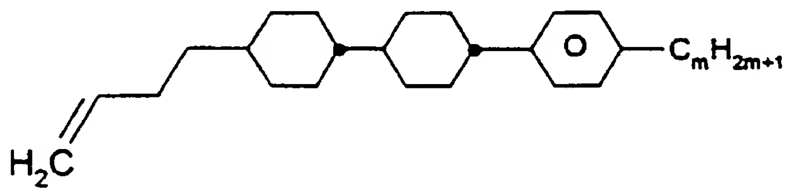

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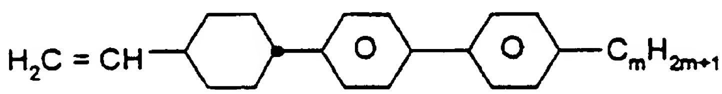

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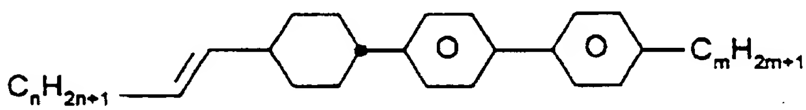

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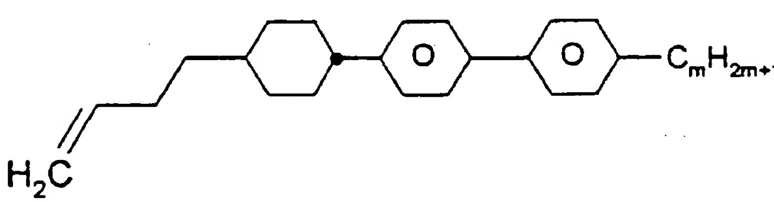

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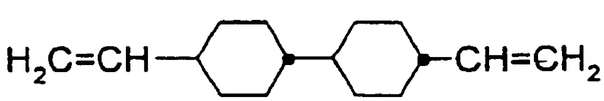
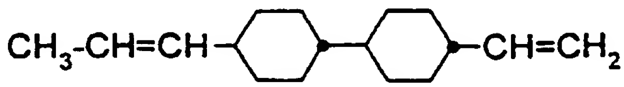


CC-V-V



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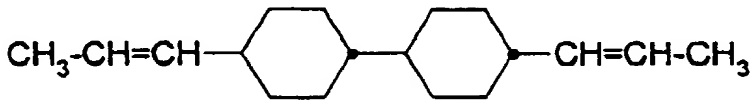

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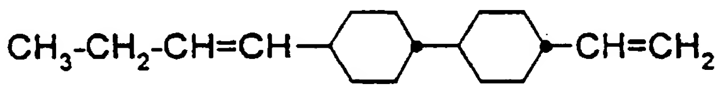
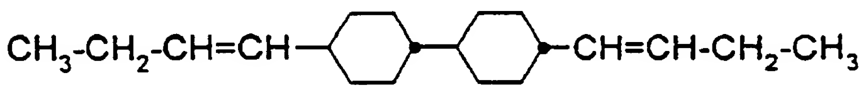


CC-2V-V



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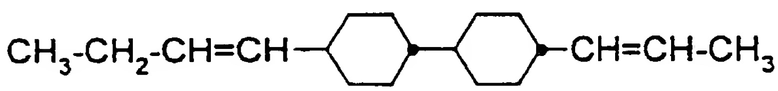
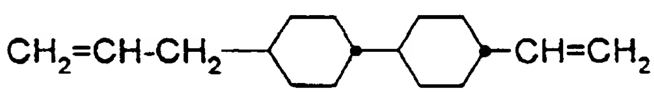


CC-2V-V1



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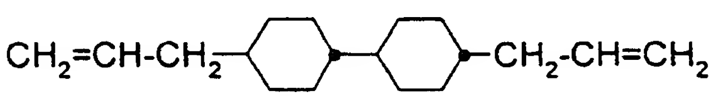
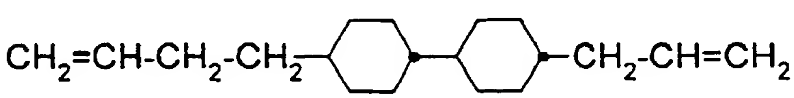
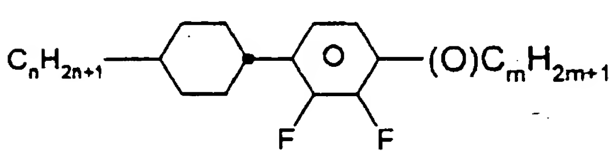


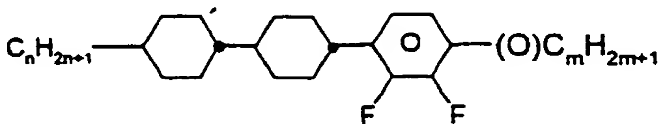
CC-V1-1V



CC-V2-1V



PCH-n(O)mFF



CCP-n(O)mFF

The examples below are intended to illustrate the invention without representing a limitation. Above and below, percentages are per cent by weight. All temperatures are given in degrees Celsius. Δn denotes the optical anisotropy (589 nm, 20°C), Δε the dielectric anisotropy (1 kHz, 20°C), H.R. the voltage holding ratio (at 100°C, after 5 minutes in an oven, 1 V), and V_{10}, V_{50} and V_{90} the threshold voltage, mid-grey voltage and saturation voltage respectively were determined at 20°C.

Example 1

	Compound/ abbreviation	Concentration/ %	Properties
	CCH-301	12.00	Clearing point = 86.5°C
	CC-5-V	6.00	Transition (S,N) < -40°C
	CH-33	4.00	V_{10} (20°C) = 1.48 V
	CH-35	4.00	V_{50} (20°C) = 1.76 V
	CCZU-2-F	6.00	V_{90} (20°C) = 2.21 V
Formel I	CCZU-3-F	16.00	d_v/d_T (0-40°C) = 1.19 mV/°
	CCZU-5-F	6.00	Δn (589 nm, 20°C) = 0.0695
	CDU-2-F	10.00	
	CDU-3-F	12.00	
	CDU-5-F	8.00	
	PCH-502FF	5.00	
Formel II	CCP-302FF	5.00	
	CCP-31FF	6.00	
		100.00	

The liquid-crystal medium was introduced into a TN-AMD display with TFT addressing. This display had good contrast with low viewing-angle dependence and was substantially free from cross-talk between adjacent on and off pixels.

Example 2

Compound/ abbreviation	Concentration/ %	Properties
CCP-2F.F.F	9.0	Clearing point = 91.0°C
CCP-3F.F.F	10.0	Transition (S,N) < -40°C
CCP-3OCF3	8.0	Δn (20°C, 589 nm) = 0.1038
CCP-5OCF3	8.0	$\Delta\varepsilon$ (20°C, 1 kHz) = 5.5
BCH-3F.F.F	12.0	$\varepsilon_{\parallel}$ (20°C, 1kHz) = 11.4
BCH-5F.F.F	11.0	$\varepsilon_{\perp}$ (20°C, 1 kHz) = 5.9
CGU-2-F	6.0	
PCH-302FF	8.0	
PCH-502FF	8.0	
CCP-302FF	9.0	1,93
CCP-502FF	8.0	
CBC-33F	3.0	
	100.00	

As in Example 1, the liquid-crystal medium was introduced into a TN-AMD display with TFT addressing. This display had good contrast with low viewing-angle dependence and was substantially free from cross-talk between adjacent on and off pixels.

Comparative Example 1

For comparison, the liquid-crystal medium disclosed in EP 0 406 468 of the following composition was prepared:

Compound/ abbreviation	Concentration/ %	Properties
PCH-5F	12.0	Clearing point = 90.0°C
PCH-6F	10.0	Transition (S,N) < -20°C
PCH-7F	10.0	Δn (20°C, 589 nm) = 0.0803
CCP-3OCF3	13.0	$\Delta\varepsilon$ (20°C, 1 kHz) = 4.3
CCP-5OCF3	12.0	$\varepsilon_{\parallel}$ (20°C, 1kHz) = 7.2
ECCP-3OCF3	11.0	$\varepsilon_{\perp}$ (20°C, 1 kHz) = 2.9
ECCP-5OCF3	9.0	
ECCP-3F.F	13.0	
CBC-33F	3.0	
CBC-53F	4.0	
CBC-55F	3.0	
	100.00	

24

The liquid-crystal medium was introduced into a TN-AMD display as in Example 2. With similar properties regarding contrast and viewing-angle dependence, significantly more pronounced cross-talk was observed in the comparative experiment.

Furthermore, the capacitance of test cells having a layer thickness of 20 μm and electrode surface areas of 1 cm^2 with earthed protective ring electrodes were investigated. To do this, the voltage was increased in 0.1 V steps from 0.1 V to 1 V, then in 20 mV steps up to 2.0 V, then again in 0.1 V steps up to 5 V and subsequently in 1 V steps up to 20 V. The results are shown in Figure 1.

Figure 1 shows the capacitance of test cells filled with liquid-crystal mixtures as a function of the applied voltage. The solid diamonds (♦) show the results for the mixture of Example 2, the open triangles (Δ) those for Comparative Example 1. Up to a limiting voltage of the dielectric or Freedericksz's threshold, the capacitance of the test cells remains constant (c_{off}). The capacitance then increases with

increasing voltage to a limit value (c_{on}). It is apparent that the mixture from Example 2 has a significantly better, i.e. smaller, c_{on}/c_{off} ratio than the mixture of the comparative example, namely a c_{on}/c_{off} of 1.9 compared with 2.3. It should be noted here that the capacitance axis in the figure must not begin at 0.

Example 3

Compound/ abbreviation	Concentration/ %	Properties
PCH-3O4FF	12.00	Clearing point = 70.5°C
PCH-5O2FF	12.00	Transition (S,N) < -40°C
PCH-5O4FF	12.00	Δn (20°C, 589 nm) = 0.0813
CCP-2O2FF	11.00	n_o (20°C, 589 nm) = 1.4761
CCP-3O2FF	11.00	K_1 (20°C) = 13.0 pN
CCP-5O2FF	10.00	K_3 (20°C) = 13.7 pN
CCP-2F.F.F	2.00	V_o (20°C) = $V_{Fr.}$ = 1.97 V
CC-5-V	3.00	d = 4 μm
CCH-34	5.00	
CCH-35	5.00	
CCPC-34	4.00	
PCH-53	13.00	
Σ	100.00	

The liquid-crystal medium was prepared and investigated in a conventional manner. It was then introduced into a VAN display with TFT addressing. This display has very good contrast and virtually no viewing-angle dependence. In addition, it is practically free from cross-talk between adjacent pixels. In addition, no flicker occurs.

The offset voltage was determined as described above. At a gate voltage (V_{gate}) of 5 V (with c_{gs} = 0.05 pF and with no storage capacitor), ΔV = 0.41 V.

Comparative Example 2

Compound/ abbreviation	Concentration/ %	Properties
PCH-3O2FF	16.00	Clearing point = 71.0°C
PCH-5O2FF	14.00	Transition (S,N) < -30°C
CCP-3O2FF	12.00	Δn (20°C, 589 nm) = 0.0822
CCP-5O2FF	11.00	n_o (20°C, 589 nm) = 1.5587
CCP-21FF	9.00	K_1 (20°C) = 13.6 pN
CCP-31FF	8.00	K_3 (20°C) = 14.7 pN
CCH-34	8.00	V_o (20°C) = $V_{Fr.}$ = 2.08 V
CCH-35	9.00	d = 4 μm
PCH-53	7.00	
PCH-3O1	6.00	
Σ	100.00	

The above liquid-crystal mixture was prepared and investigated analogously to the liquid-crystal mixtures from Example 3. This liquid-crystal mixture is dielectrically negative like that of Example 3. However, in contrast thereto, it contains no dielectrically positive compounds.

Although the liquid-crystal mixture of this Comparative Example 2 generally has similar properties to that of Example 3, it is inferior thereto in virtually all applicationally relevant properties, for example in contrast, viewing-angle dependence, in particular in the operating voltage (threshold voltage) and most clearly in the occurrence of cross-talk and flicker in VAN displays.

The offset voltage was determined as described in Example 3. At a gate voltage (V_{gate}) of 5 V (with c_{gs} = 0.05 pF and with no storage capacitor), ΔV = 0.45 V.

Example 4

Compound/ abbreviation	Concentration/ %	Properties
CCP-3O2FF	12.00	Clearing point = 89.0°C
CCP-5O2FF	12.00	Transition (S,N) < -30°C
BCH-3F.F.F	14.00	Δn (20°C, 589 nm) = 0.1622
BCH-5F.F.F	10.00	n_o (20°C, 589 nm) = 1.4902
CGU-2-F	16.00	$\Delta\varepsilon$ (20°C, 1 kHz) = 11.3
CGU-3-F	14.00	$\varepsilon_\perp$ (20°C, 1 kHz) = 6.3
CGU-5-F	14.00	$d\cdot\Delta n$ = 0.55 μm
CCGU-3-F	8.00	λ = 550 nm
		ϕ = 90°S
		V_{10} (20°C) = 1.270
		V_{90} (20°C) = 2.04
Σ	100.00	

Example 5

Composition	Concentration/ %	Properties
CCP-2F.F.F	9.0	Clearing point = +91.0°C
CCP-3F.F.F	10.0	Δn = + 0.1038
CCP-3OCF3	8.0	n_o (589.3 nm, 20°C) = 1.4808
CCP-5OCF3	8.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 5.5
BCH-3F.F.F	12.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.9
BCH-5F.F.F	11.0	K_1 (20°C) = 12.1 pN
CGU-2-F	6.0	K_3 (20°C) = 15.3 pN
PCH-3O2FF	8.0	V_0 (20°C) = 1.57 V
PCH-5O2FF	8.0	
CCP-3O2FF	9.0	
CCP-5O2FF	8.0	
CBC-33F	3.0	
Σ	100.0	

Example 6

Composition	Concentration/ %	Properties
PCH-502FF	6.0	Clearing point = + 90.0°C
CCP-302FF	10.0	Δn = + 0.0919
CCP-502FF	10.0	n_o (589.3 nm, 20°C) = 1.4794
CCP-21FF	8.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 4.2
CCP-2OCF3	5.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.4
CCP-3OCF3	2.0	
CCP-2F.F.F	8.5	
CCP-3F.F.F	8.5	
CGU-2-F	12.0	
CGU-3-F	10.0	
CC-5-V	13.5	
CCH-35	3.5	
CBC-33F	3.0	
Σ	100.0	

5.4
1.2

Example 7

Composition	Concentration/ %	Properties
PCH-5O2FF	6.0	Clearing point = + 109.0°C
CCP-3O2FF	6.0	Δn = + 0.0957
CCP-5O2FF	12.0	n_o (589.3 nm, 20°C) = 1.4767
CCP-21FF	10.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 4.8
CCP-31FF	6.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.5
CCP-2OCF3	4.0	
CCP-3OCF3	4.0	
CCP-4OCF3	6.0	
CCP-5OCF3	6.0	
CCP-2F.F.F	8.0	
CCP-3F.F.F	8.0	
CCP-5F.F.F	4.0	
CGU-3-F	7.0	
CGU-5-F	10.0	
CCH-35	3.0	
Σ	100.0	

Example 8

Composition	Concentration/ %	Properties
PCH-5O2FF	6.0	Clearing point = + 90.0°C
CCP-3O2FF	12.0	Δn = + 0.0956
CCP-5O2FF	12.0	n_o (589.3 nm, 20°C) = 1.4798
CCP-21FF	4.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 3.2
CCP-2OCF3	6.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.5
CCP-3OCF3	6.0	K_1 (20°C) = 13.4 pN
CCP-4OCF3	6.0	K_2 (20°C) = 6.5 pN
CCP-2F.F.F	6.0	K_3 (20°C) = 16.8 pN
CCP-3F.F.F	10.0	
CGU-2-F	10.0	
CGU-3-F	2.0	
BCH-32F	2.0	
PCH-3O2	18.0	
Σ	100.0	

Example 9

Composition	Concentration/ %	Properties
PCH-5O2FF	6.0	Clearing point = + 91°C
CCP-3O2FF	8.0	Δn = + 0.0955
CCP-5O2FF	12.0	n_o (589.3 nm, 20°C) = 1.4791
CCP-21FF	6.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 4.9
CCP-2OCF3	4.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.4
CCP-3OCF3	6.0	K_1 (20°C) = 12.3 pN
CCP-4OCF3	6.0	K_2 (20°C) = 6.4 pN
CCP-2F.F.F	8.0	K_3 (20°C) = 16.3 pN
CCP-3F.F.F	8.0	
CCP-5F.F.F	6.0	
CGU-3-F	8.0	
CGU-5-F	10.0	
PCH-3O2	12.0	
Σ	100.0	

Example 10

Composition	Concentration/ %	Properties
PCH-5O2FF	6.0	Clearing point = + 91.0°C
CCP-3O2FF	10.0	Δn = + 0.0909
CCP-5O2FF	10.0	n_o (589.3 nm, 20°C) = 1.4784
CCP-21FF	8.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 3.7
CCP-2OCF3	4.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.3
CCP-3OCF3	6.0	
CCP-4OCF3	6.0	
CCP-2F.F.F	8.0	
CCP-3F.F.F	9.0	
CCP-5F.F.F	6.0	
CGU-3-F	6.0	
CGU-5-F	10.0	
PCH-53	8.0	
CC-5-V	3.0	
Σ	100.0	

Example 11

Composition	Concentration/ %	Properties
PCH-5O2FF	8.0	Clearing point = + 81.0°C
CCP-3O2FF	9.0	Δn = + 0.0907
CCP-5O2FF	9.0	n_o (589.3 nm, 20°C) = 1.4790
CCP-21FF	7.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 4.3
CCP-2OCF3	3.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.3
CCP-3OCF3	6.0	
CCP-4OCF3	5.0	
CCP-2F.F.F	8.0	
CCP-3F.F.F	9.0	
CCP-5F.F.F	6.0	
CGU-3-F	6.0	
CGU-5-F	9.0	
PCH-53	9.0	
PCH-3O2	6.0	
Σ	100.0	

Example 12

Composition	Concentration/ %	Properties
PCH-5O2FF	5.0	Clearing point = + 81.3°C
CCP-3O2FF	6.0	Δn = + 0.0682
CCP-5O2FF	6.0	n_o (589.3 nm, 20°C) = 1.4741
CCH-3O1	8.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 4.8
CCH-5O1	4.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 4.6
CC-5-V	14.0	
PCH-7F	5.0	
CCP-2F.F.F	8.0	
CCP-3F.F.F	11.0	
CCP-5F.F.F	5.0	
CCZU-2-F	5.0	
CCZU-3-F	15.0	
CCZU-5-F	5.0	
CH-33	1.5	
CH-43	1.5	
Σ	100.0	

Example 13

Composition	Concentration/ %	Properties
PCH-5O2FF	6.0	Clearing point = + 90.0°C
CCP-3O2FF	12.0	Δn = + 0.0956
CCP-5O2FF	12.0	n_o (589.3 nm, 20°C) = 1.4798
CCP-21FF	4.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 3.2
CCP-2OCF3	6.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.5
CCP-3OCF3	6.0	K_1 (20°C) = 13.4 pN
CCP-4OCF3	6.0	K_2 (20°C) = 6.5 pN
CCP-2F.F.F	6.0	K_3 (20°C) = 16.8 pN
CCP-3F.F.F	10.0	
CGU-2-F	10.0	
CGU-3-F	2.0	
BCH-32F	2.0	
PCH-3O2	18.0	
Σ	100.0	

Example 14

Composition	Concentration/ %	Properties
PCH-5O2FF	6.0	Clearing point = + 91.0°C
CCP-3O2FF	8.0	Δn = + 0.0955
CCP-5O2FF	12.0	n_o (589.3 nm, 20°C) 1.4791
CCP-21FF	6.0	$\Delta\varepsilon$ (1 kHz, 20°C) = 4.9
CCP-2OCF3	4.0	$\varepsilon_\perp$ (1 kHz, 20°C) = 5.5
CCP-3OCF3	6.0	K_1 (20°C) = 12.3 pN
CCP-4OCF3	6.0	K_2 (20°C) = 6.4 pN
CCP-2F.F.F	8.0	K_3 (20°C) = 16.3 pN
CCP-3F.F.F	8.0	
CCP-5F.F.F	6.0	
CGU-3-F	8.0	
CGU-5-F	10.0	
PCH-3O2	12.0	
Σ	100.0	